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(54) Title: METHOD AND APPARATUS FOR THE MEASUREMENT OF DISSOLVED CARBON

(57) Abstract

Apparatus and methods for the measurement of total organic carbon, total inorganic carbon and total carbon of water are described. The sample is acidified and split into an inorganic carbon stream and a total carbon stream. The inorganic carbon in the inorganic stream is oxidized using an oxidizer potential that varies over an oxidizer potential period, and both the organic carbon in the total carbon stream are oxidized. The resulting carbon dioxide is measured in each stream using carbon dioxide sensors employing a gas permeable membrane dividing deionized water from the oxidized sample water and a pair temperature and conductivity cells.

METHOD AND APPARATUS FOR THE MEASUREMENT
OF DISSOLVED CARBON

5   This application is a continuation-in-part of
application no. 08/501,597 filed July 12, 1995 which is a
continuation-in-part of application no. 07/869,308 filed
April 16, 1992, which is a divisional of application no.
07/487,720 filed March 2, 1990, the contents of both of
10   which are hereby incorporated by reference.

Field of the Invention

          The present invention relates to an improved
method and apparatus for the determination of the
15   concentration of organic carbon, inorganic carbon and
total carbon in aqueous process streams and in bulk
solutions. Particularly, the method of the present
invention in a preferred embodiment includes the
acidification of an aqueous sample stream, the oxidation
20   of the sample stream to produce dissolved carbon dioxide
gas, and the sensitive and selective detection of carbon
dioxide utilizing a gas permeable membrane and
conductometric detection to determine the levels of
organic carbon, inorganic carbon and/or total carbon.

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Background of the Invention

          The measurement of the total organic carbon
(TOC) concentration and total carbon (organic plus
inorganic) concentration in water has become a standard
30   method for accessing the level of contamination of
organic compounds in potable waters, industrial process
waters, and municipal and industrial waste waters. In
addition to widespread terrestrial applications, the

2

measurement of TOC is one of the primary means of
determining the purity of potable and process waters for
manned space based systems including the space shuttle,
the proposed space station and for future manned

5   explorations of the moon and planets.

The United States Environmental Protection
Agency recently promulgated new rules aimed at reducing
the levels of disinfectant by-products in drinking water.
Formed from the reaction of chlorine and other

10   disinfectants with naturally occurring organic matter,
disinfectant by-products are potentially hazardous
compounds. Such compounds include trihalomethanes
($CHCl_3$, $CHBrCl_2$, etc.), haloacetic acids, and other
halogenated species. The new rules also include

15   monitoring the levels of natural organic material in raw
water, during the treatment process and in the finished
water by measurement of total organic carbon
concentration.

A variety of prior art approaches for measuring

20   the total organic carbon content of water have been
proposed. For example, See United States Patent Nos.
3,958,941 of Regan; 3,224,837 of Moyat; 4,293,522 of
Winkler; 4,277,438 of Ejzak; 4,626,413 and 4,666,860 of
Blades et al.; and 4,619,902 of Bernard.

25   Representative of the devices described in
these references are the methods disclosed in United
States Patent No. 3,958,941 of Regan. In Regan an
aqueous sample is introduced into a circulating water
stream that flows through a reaction chamber where the

30   sample is mixed with air and exposed to ultraviolet
(U.V.) radiation to promote the oxidation of organic

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compounds to form carbon dioxide. The carbon dioxide formed in the reaction chamber is then removed from solution by an air stripping system and introduced into a second chamber containing water that has been purified to remove ionic compounds. The conductivity of the water in the second chamber is measured, and any increase in conductivity is related to the concentration of carbon dioxide formed in the first reactor. The conductivity measurement can be used, therefore, to determine the concentration of organic compounds in the original sample.

The Regan device is slow, cannot be used for the continuous monitoring of TOC concentration in aqueous streams, cannot be scaled down without increasing interference from NO_2, SO_2, and H_2S to unacceptable levels, and is generally unsatisfactory. In addition, Regan does not disclose that an aqueous solution of acid must be added to the sample stream to reduce the pH to a value of less than about 4 to ensure a reasonable removal rate of carbon dioxide using the air stripping system described. The oxidation method disclosed by Regan is unsatisfactory for the measurement of refractory compounds, particularly urea. In Regan, an aqueous sample of 20 to 100 mL containing 0.5 mg/L organic carbon is required to generate sufficient carbon dioxide for accurate detection, thus limiting the utility of the device for the measurement of sub-part per million levels of TOC in smaller sample sizes. Finally, in practice, the Regan system requires frequent recalibration-- typically once per day--due to variations in background conductivity. Also, the concentration of organic carbon

4

in the calibration standard must be approximately equal
to the concentration of organic carbon in the sample.
Because of this, recalibration is required when analyzing
aqueous samples containing higher or lower levels of
5   organic carbon when compared with the calibration
standard.

The use of aqueous solutions of persulfate
salts for the oxidation of organic compounds is widely
known. Smit and Hoogland (16 Electrochima Acta, 1-18
10   (1971)) demonstrate that persulfate ions and other
oxidizing agents can be electrochemically generated. In
United States Patent No. 4,504,373 of Mani et al., a
method for the electrochemical generation of acid and
base from aqueous salt solutions is disclosed.

15   An improved method and apparatus for the
measurement of organic content of aqueous samples is
disclosed in United States Patent No. 4,277,438 of Ejzak.
Ejzak describes a multistage reactor design which
provides for the addition of oxygen and a chemical
20   oxidizing agent, preferably sodium persulfate, to the
aqueous sample stream prior to oxidation of the stream
using ultraviolet radiation in a series of reactors.
Ejzak also describes the use of an inorganic carbon
stripping process--before oxidation of the organic
25   carbon--that includes the addition of phosphoric acid to
the sample stream. After oxidation, the sample stream is
passed into a gas-liquid separator where the added oxygen
acts as a carrier gas to strip carbon dioxide and other
gases from the aqueous solution. In the preferred
30   embodiment, the gas stream is then passed through an acid
mist eliminator, a coalescer and salt collector, and

through a particle filter prior to passage into an
infrared (IR) detector for the measurement of the
concentration of carbon dioxide in the gas stream.

The methods and apparatus disclosed by Ejzak
provide improvements over the teachings of Regan;
however, the Ejzak device requires extensive manual
operation and is also generally unsatisfactory. The
Ejzak device requires three external chemical reagents;
oxygen gas, aqueous phosphoric acid and an aqueous
solution of sodium persulfate. Both the phosphoric acid
and persulfate solutions must be prepared at frequent
intervals by the operator due to the relatively high rate
of consumption. The Ejzak device requires dilution of
the sample if the solution contains high concentrations
of salts in order to ensure complete oxidation of the
sample and to eliminate fouling of the particle filter
located prior to the IR carbon dioxide detector. As with
Regan, relatively large sample sizes are required--
typically 20 mL of sample for accurate measurement at 0.5
mg/L total organic carbon--and the carbon dioxide formed
in the oxidation chamber is removed using a gravity
dependent technique that cannot be easily used in space-
based operations.

Another improved method and apparatus for the
measurement of total organic carbon in water is disclosed
in United States Patent No. 4,293,522 of Winkler. In
Winkler, an oxidizing agent, molecular oxygen, is
generated in-situ by the electrolysis of water. Organic
compounds are subsequently oxidized to form carbon
dioxide by the combination of U.V. radiation and the in-
situ generated oxygen. The irradiation and electrolysis

processes are both accomplished in a single oxidation
chamber. Winkler does not teach that the aqueous sample
stream be acidified to assist in the removal of carbon
dioxide from solution, and in fact teaches against the
5   use of acid. Therefore, this method and apparatus cannot
be used for the measurement of organic compounds in basic
aqueous samples. The oxidation chamber of Winkler uses a
solid electrolyte to separate the two electrodes employed
for the electrolysis of water. The solid electrolyte
10   described by Winkler is composed of an organic polymer
which, under exposure to oxygen, ozone and U.V.
radiation, will undergo oxidation to form carbon dioxide,
therefore resulting in unacceptable background levels of
organic compounds in the sample stream, particularly at
15   low organic compound concentrations.

         Winkler also describes a conductometric carbon
dioxide detection system wherein the sample stream
exiting the oxidizing chamber is held in an equilibrating
relationship to a stream of deionized water. The two
20   flowing streams are separated by a gas permeable membrane
that allows the concentration of carbon dioxide to
equilibrate between the streams. The concentration of
the carbon dioxide is thereby determined by measuring the
conductance of the deionized water stream. However, the
25   use of two flowing streams introduces operating
parameters into the detection process that require
frequent calibration adjustments. The recirculation of
deionized water with dissolved carbon dioxide can cause a
diffusion of the carbon dioxide out of the deionized
30   water into plastic components of the recirculation loop,
and cause the introduction of ionic contamination into

the deionized water. Further, the Winkler process is a very time-consuming batch process which is not commercially practical.

Another example of the prior art is disclosed in United States Patent No. 4,619,902 of Bernard, which teaches the oxidation of organic compounds to form carbon dioxide using persulfate oxidation at elevated temperatures--typically 20 to 100°C--in the presence of a platinum metal catalyst. Bernard recognizes that the materials used in the construction of instrumentation for the determination of total organic carbon in water can contribute organic compounds to the sample during the measurement process, and teaches that inert materials such as PTFE must be used to reduce this background from the measurement. As with the previously mentioned disclosures, a gas stripping technique is employed to collect the formed carbon dioxide, and measurement is made using IR spectrometry. Bernard also recognizes that aqueous solutions of sodium persulfate are not stable due to auto-degradation of the reagent.

An improved system for the measurement of organic compounds in deionized water is disclosed in United States Patent No. 4,626,413 of Blades and Godec. The apparatus described by Blades and Godec is based on direct U.V. oxidation of organic compounds to form carbon dioxide which is measured by using conductometric detection. In the apparatus described in Blades and Godec, the oxidation of some organic compounds form strong acids such as HCl, H_2SO_4 and HNO_3 which interfere with the conductometric method. The Blades device is also limited to the measurement of total organic

8

compounds in deionized water and cannot be used for
samples containing ionic compounds other than bicarbonate
ion.

In United States Patent No. 4,209,299 of
Carlson, it is disclosed that the concentration of
volatile materials in a liquid can be quantitively
determined by transferring the desired material through a
gas permeable membrane into a liquid of known
conductivity, such as deionized water. The Carlson
device is demonstrated for the measurement of a number of
volatile organic and inorganic compounds, but Carlson
does not suggest the combination of this process in
conjunction with a carbon dioxide producing reactor.

In electrochemical reactions in aqueous
solutions, a common reduction product is hydrogen gas.
Because of its flammability, the hydrogen presents a
potential hazard in devices using electrochemical
techniques. Hydrogen gas in solution with water in the
presence of U.V. light will reduce organics; thus, the
hydrogen must be removed in some manner to ensure the
oxidation of organics in the presence of U.V. light. The
interaction of hydrogen gas in aqueous solutions and
palladium metal is well known (e.g., F.A. Lewis, "The
Palladium Hydrogen System," Academic Press, 1967, London)
and the use of palladium offers a potential solution to
the generation of hydrogen in electrochemical reactions
by selective removal and disposal of the hydrogen.

An improved carbon analyzer is disclosed in
U.S. Patent No. 5,132,094 by Godec et al., of which the
present is a continuation-in-part. Originally developed
for NASA, the Godec device uses UV/persulfate oxidation

and a new CO_2 detection technique utilizing a gas-permeable membrane and a temperature and conductivity cell. A gas-permeable membrane is used to separate the acidified sample stream (pH<4) from a thin layer of

5   deionized water. A solenoid valve is opened to allow fresh DI water to flow into the membrane module and the solenoid valve is closed. Carbon dioxide formed from the oxidation of organic compounds will diffuse across the membrane into the deionized water, where a portion of the

10   CO_2 will ionize to produce H+ and HCO_3-ions. After an equilibration period, the solenoid valve is opened to flush the ions into a conductivity and temperature measurement cell, and the concentration of CO_2 in the deionized water is determined from the conductivity and

15   temperature.

Membrane-based conductivity detection of CO_2 offers several advantages. Calibration is extremely stable, and the calibration can be easily performed by the analyst. No purge gases are required. The technique

20   is highly selective for CO_2 and is extremely sensitive, permitting detection of TOC down to sub-parts per billion levels. It also has a wide dynamic range, permitting measurement up to at least 100 ppm TOC.

In operation the sample is drawn into the

25   analyzer by means of a peristaltic pump, and two reagents are added via syringe pumps. Acid (6 M H_3PO_4) is added to reduce the pH of the sample stream and persulfate (15% $(NH_4)_2S_2O_8$) is added for the oxidation of organic compounds. The sample stream is split for measurement of

30   inorganic carbon (IC) concentration (IC=$[HCO_3-]$ + $[CO_3-^2]$+$[CO_2]$) without oxidation, and measurement of total

carbon (TC) concentration after oxidation. TOC is then computed from the difference (TOC=TC-IC). For samples containing high levels of inorganic carbon and lower levels of TOC, an IC removal module may be used to remove

5   the inorganic carbon and permit accurate TOC measurements. A supply of the acid and oxidizer may be pre-packaged and stored in the analyzer, eliminating the need for reagent preparation by the analyst. Deionized water is continuously produced in the analyzer using a

10   mixed-bed ion exchange resin with a capacity for several years of operation. The maintenance required is replacement of the reagent containers several times a year, replacement of the UV lamp and replacement of the pump tubing. The ease of use, low maintenance

15   requirements and dependable performance have made this device the TOC analyzer of choice for monitoring water purification systems in semiconductor manufacturing, the pharmaceutical industry and both conventional and nuclear power plants.

20   It is important that the amount of persulfate or other oxidizer added to the sample be sufficient to fully oxidize the sample. However, it is also important not to add excess oxidizer to the point that gas bubbles form in the sample. Gas bubbles are undesirable because

25   the carbon dioxide dissolved in the sample will diffuse into the oxygen bubbles. Further, if the oxygen bubble diffuses through the membrane and into the deionized water stream, the result will be a negative spike in the measured conductivity as the bubble passes through the

30   conductivity cell and partially or wholly insulates the conductivity electrode from the water stream.

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This has been addressed in the past by controlling the addition of oxidizer based on the expected approximate range of carbon concentration. For example, the oxidizer flow rate would be set relatively low if the expected carbon concentration were in the 1 to 5 ppm range, and the oxidizer flow rate would be set higher if the expected carbon concentration were in the 25 to 50 ppm range. This is a simple and very effective approach. However, it would be desirable for the device to produce accurate readings across a broad range of carbon concentrations with a minimum of experimentation or prior knowledge about the approximate expected carbon concentrations.

It has also been found in utilizing prior devices that chloride in the sample tends to lead to inaccurate measurements of carbon concentrations, because the chloride preferentially interacts with hydroxyl radicals to the exclusion of organics, thus exhausting the oxidizer before the organics are fully oxidized.

Summary of the Invention

An important aspect of the invention which is common to each of the preferred embodiments is varying over a period of time the oxidation potential used to oxidize a sample. By so varying the oxidation potential, there is assurance that at some point in the oxidation potential period the sample becomes substantially completely oxidized without the formation of oxygen bubbles. The measured conductivity of the sample is at a peak at that point and can be accurately related to the true carbon concentration.

12

In one embodiment of the present invention, an
aqueous sample stream is passed through a filter to
remove any particulate matter. Acid is added to produce
a pH of less than 4. Inorganic carbon species--primarily
5   carbonate and bicarbonate ions--are reacted with the acid
to form carbon dioxide, while organic compounds remain
unreacted. Also added is an oxidizer such as persulfate.

The sample is then split into a first stream
for measurement of total carbon and a second stream for
10   measurement of inorganic carbon. The first stream is
directed into an oxidation module for oxidation of
organic compounds into carbon dioxide. The oxidation
module may incorporate either direct U.V. oxidation using
short wavelength U.V. radiation such as an excimer source
15   or a mercury vapor lamp, semiconductor catalyzed U.V.
oxidation using short wavelength U.V. radiation, or U. V.
oxidation in the presence of oxygen and or other
oxidizing agents. The U.V. radiation may be generated
particularly well using a narrow band excimer source.

20   The degree of oxidation potential in the
oxidation module is not constant over time. Instead, the
oxidation is done in cycles in which the oxidation
potential changes from near zero to a maximum, gradually
over a period of time such as three or four minutes. By
25   gradually increasing the oxidation potential over a timed
cycle, there is assurance that the optimum oxidation
potential, and thus the optimum overall oxidation, is
achieved at some point in the cycle. The term "oxidation
potential" is used herein to mean the potential for
30   oxidation of a compound due to the presence of an
oxidation source. The oxidation source may be a chemical

reagent such as persulfate and/or other means such as an
electrolysis cell or U.V. light. The oxidation potential
is varied by increasing or decreasing the concentration
of a chemical oxidizer, or increasing or decreasing the

5   activity of the other possible means such as the rate of
oxygen generation in an electrolysis cell or the
intensity of a U.V. light source or the duration of the
U.V. light exposure.

       The carbon dioxide formed in the oxidation

10   module is sensitively measured using a carbon dioxide
sensor. The sensor includes a first gas-transfer module
which is comprised of a carbon dioxide selective gas-
permeable membrane which separates the first stream from
a deionized water stream. The deionized stream is in a

15   closed loop and is continuously regenerated by means of a
mixed bed ion exchange resin. Alternatively, deionized
water can be supplied from a source external to the
apparatus described in the present invention. The
deionized water in one embodiment may be maintained at a

20   positive pressure such as approximately 5-6 PSI higher
than the first stream pressure to inhibit bubble
formation in the deionized water.

       As the carbon dioxide enters the deionized
water, the carbon dioxide will dissolve in the water and

25   cause an increase in the conductivity of the aqueous
solution. The stream of deionized water with dissolved
carbon dioxide then flows out of the first gas transfer
module and into a temperature and conductivity cell in
order to measure the increase in the concentration of

30   ionic species. There is a passive deoxygenation module
in the deionized water loop to remove oxygen gas from the

water after it passes through the temperature and conductivity cell on its way to the next pass into the first gas transfer module.

The peak conductivity observed in the deionized water with dissolved carbon dioxide during any given oxidation potential cycle can be directly related to the concentration of carbon dioxide in the first stream. The concentration of carbon dioxide in the first stream can, in turn, be directly related to the level of organic compounds originally present in the sample.

The second stream flows simultaneous with the flow of the first stream. The second stream first flows through a delay tubing to compensate for the period of time the first stream is in the oxidation module. The second carbon stream then flows through its own separate carbon dioxide sensor which functions similarly to the carbon dioxide sensor for the first stream. However, because there is no oxidation step in the second stream, organic carbon remains unoxidized and therefore undetected. The entire detected carbon in the second stream can be presumed to be inorganic carbon. The device thus accurately measures both total carbon and inorganic carbon. Total organic carbon can be determined by subtracting the inorganic carbon measurement from the peak total carbon measurement in a given oxidation potential cycle.

In the preferred embodiment, the device utilizes components with very small volumes and water layer thicknesses. This is important in facilitating rapid response times and sensitivities.

Other embodiments are possible utilizing the approach of varying the oxidation potential over an oxidation potential period. In an exemplary alternative embodiment, inorganic carbon is measured in an inorganic
5   carbon measurement step, and then organic carbon is measured in an organic carbon measurement step. The inorganic carbon measurement step includes acidifying the sample stream to convert inorganic carbon to carbon dioxide. The sample stream with dissolved carbon dioxide
10   then flows into a first gas transfer module for the transfer of carbon dioxide to a deionized water stream and measurement of conductivity in a first temperature and conductivity cell. That measurement can be related to the inorganic carbon concentration in the sample.

15   The stream then flows into a carbon dioxide degassification module or other carbon dioxide removal device, in which the stream is contained within a gas-permeable conduit or container surrounded by a vacuum. The dissolved carbon dioxide produced by earlier
20   acification of the stream is thus removed from the stream.

The organic carbon in the stream is then oxidized using an oxidation potential that varies over an oxidation potential cycle. As in the other embodiments,
25   the variation in the oxidation potential can be accomplished by varying the rate of introduction of a chemical reagent, or by other means as described herein. The stream then flows into a second gas transfer module for the transfer of carbon dioxide into a deionized water
30   stream and measurement of conductivity in a second temperature and conductivity cell. This measurement can

be related to the organic carbon concentration in the sample.

This alternative embodiment thus provides a means to measure both inorganic carbon and organic carbon. Total carbon can be determined by adding the two measurements.

Brief Description of the Drawings

FIG. 1 is a block diagram depicting an embodiment of the present invention for the on-line measurement of carbon concentrations in accordance with the present invention.

FIG. 2 is a representation of the measured carbon in a sample using variable oxidation potential.

FIG. 3 is a graph of measured carbon and persulfate oxidizer flow rate versus time for a preferred embodiment of the invention.

FIG. 4 is a block diagram depicting an alternative embodiment of the present invention for the on-line measurement of carbon concentrations.

Detailed Description of the Preferred Embodiment

The measurement of the total organic content of aqueous samples has become a standard technique for determining the quality of potable water, industrial process water and industrial and municipal waste waters. The determination of the organic content of water samples is most commonly achieved by oxidation of the carbon constituents to carbon dioxide using chemical oxidizing agents, U.V. radiation, electrolysis, high temperature combustion, or a combination of these methods and

subsequent detection of the carbon dioxide using IR spectroscopy or by membrane/conductometric or potentiometric techniques. The present invention is an improved process and apparatus for determining concentration levels of total organic and inorganic carbon compounds in aqueous samples.

A block diagram of one embodiment of the present invention is shown in FIG. 1. An aqueous sample inlet 10 is in communication with a particle filter 12 for the removal of particulate matter that may be suspended in the aqueous sample stream. A filter outlet conduit 14 joins a fitting 16. An acid reagent (6 M H_3PO_4 in the preferred embodiment) is delivered to the fitting 16 via a pump such as the acid syringe pump 20 shown in FIG. 1 through an acid line 22. The acid syringe pump 20 is driven by a motor 24 and worm gear 26 in the manner well known in the field of syringe pumps. An oxidizer reagent (15% $(NH_4)_2S_2O_8$) is delivered to the fitting 16 via another pump such as the oxidizer syringe pump 28 shown in FIG. 1 through an oxidizer line 30. The oxidizer syringe pump 28 is also driven by a motor 32 and worm gear 34 in the conventional manner. The apparatus may include an acid reservoir (not shown) for periodic replenishment of the acid syringe pump 20 and an oxidizer reservoir (not shown) for periodic replenishment of the oxidizer syringe pump 28.

The aqueous outlet conduit 40 from the fitting 16 is split into a conduit 142 for the measurement of inorganic carbon and a conduit 42 for the measurement of total carbon. It is noted that a vacuum degasser or other carbon dioxide removal device may be placed in or

near the conduit 40 to remove gas from the sample stream
which may interfere with the downstream carbon
measurements. The conduit 42 leads to a U.V. oxidation
reactor 46. Several U.V. oxidation reactors are

5   described in detail in U.S. Patent No. 5,132,094 by
Godec, of which the present is a continuation-in-part and
the contents of which are hereby incorporated by
reference. Briefly, the aqueous sample inlet of the U.V.
oxidation module is in communication with a coiled fused

10   silica tube with an internal diameter of approximately
1mm. The radius of the coil is such that a U.V.
radiation source can be positioned in the annular region
of the fused silica coiled tube. A suitable power supply
and electrical connections (not shown) are used for the

15   operation of the U.V. radiation source, which may consist
of any known device which emits U.V. radiation, such as
an excimer lamp, a gas discharge tube or a mercury vapor
discharge tube. An excimer lamp emitting light
concentrated around 172 nm or other desired excimer-

20   emitting frequencies may be particularly useful. The
design of the U.V. oxidation module has been demonstrated
to provide high efficiency conversion of organic
compounds to form carbon dioxide from aqueous samples at
concentrations up to about at least 100 mg/L total

25   organic carbon without sample dilution, with the addition
of oxygen or other chemical oxidizing reagents such as
persulfate.

The U.V. oxidation module outlet conduit 52 is
in communication with the aqueous sample inlet of the

30   first gas transfer module 56. The first gas transfer
module contains a carbon dioxide gas permeable membrane

58 positioned such that the flowing aqueous sample stream passes on one side. On the other side flows deionized water. The deionized water on the deionized water side of the membrane 58 preferably is in a thin layer of approximately 0.01 to 0.02 inch and has a total volume of less than 150 ul in the preferred embodiment. Although somewhat thicker layers and larger volumes may be used, this thin layer and small volume are important in facilitating rapid analysis and response times.

The deionized water portion consists of a mixed bed 66 of anion and cation ion exchange resins in communication via a conduit 68 with a circulating pump 70 which is in communication via a conduit 72 to a joint 74. One outlet of the joint 74 is in communication via conduit 76 with the deionized water inlet of the first gas transfer module 56. Another outlet of the joint 74 is in communication with the ion exchange resin bed 66 through conduit 78, restrictor 104 and conduit 82. Restrictor 104 is used to maintain a pressure differential of 6-7 psi on the side of the first and second gas transfer modules 56 and 156. The last outlet of the joint 74 is in communication via conduit 80 with the deionized water inlet of the second gas transfer module 156 as described below.

The deionized water outlet of the first gas transfer module 56 is in communication via a conduit 92 to the inlet of a first temperature and conductivity cell 94. As in the case of the first and second gas transfer modules 56 and 156, the dimensions and liquid volume of the first and second temperature and conductivity cells 94 and 194 are very small in the preferred embodiment --

less than 10 ul -- to ensure rapid analysis and response times. The outlet of the first temperature and conductivity cell 94 is in communication via a conduit 96 to a restrictor/deoxygenation module 98.

5   The restrictor/deoxygenation module 98 is a length of gas-permeable tubing. Any gas in the deionized water tends to permeate through the tubing and out of the water. The tubing also serves as a restrictor to maintain a pressure differential of 6-7 psi between the

10   deionized water and the sample in first and second gas transfer modules 56 and 156 and to control the flow of deionized water in the deionized water loop. Therefore, gas that may tend to be in bubble form in the sample is more likely to remain dissolved in the deionized water

15   stream. A pressure source may also be added to the deionized water stream to maintain this pressure differential, although the circulating pump 70 alone may be sufficient by properly sizing restrictor 104.

The aqueous sample outlet conduit 108 of the

20   first gas transfer module 56 is in communication with the inlet of a peristaltic sampling pump 110, and the outlet of the sampling pump is connected via a conduit 112 to a suitable waste container (not shown).

The conduit 142 for the measurement of

25   inorganic carbon leads to a coil of delay tubing 146. The purpose of the delay tubing 146 is to delay the sample flow for a period equal to the delay produced by the sample flowing through the U.V. oxidation reactor 46 on the total carbon side of the device. Therefore, the

30   delay tubing 146 is simply a coil of inert tubing. The outlet of the delay tubing 146 is in communication with a

conduit 152 leading to the second gas transfer module
156. The second gas transfer module 156 is similar to
the first gas transfer module 56. A gas permeable
membrane 158 is positioned such that the flowing aqueous
sample stream passes on one side, and deionized water
passes in the opposite direction on the other side.
Again, the deionized water is in a thin layer of
approximately 0.01 to 0.02 inches, and the chamber volume
is less than 150 ul, to facilitate rapid analysis times
in the preferred embodiment. Upon leaving the second gas
transfer module 156 via conduit 208, the sample is drawn
into sample pump 110 and discarded to a waste container
via conduit 112.

The deionized water loop for the inorganic
carbon side is similar to the deionized water loop for
the total carbon side. It includes the same ion exchange
resin bed 66, circulating pump 70, and joint 74. The
last outlet conduit 80 from the joint 74 is in
communication with the deionized water inlet of the
second gas transfer module 156. From the second gas
transfer module 156, the deionized water flows through a
conduit 192 and into a second temperature and
conductivity cell 194. The deionized water then flows
through a conduit 196, through a restrictor 198 or, if
desired, restrictor/deoxygenator, and joins the other
deionized water loop for return to the mixed bed 66.

The temperature and conductivity cells 94 and
194 are connected to a suitable power supply (not shown)
and the electrical output from the temperature and
conductivity cells 94 and 194 are connected to a control
and signal electronics module (not shown). The control

and electronic module is comprised of a computer or other
electronic device which is capable of controlling the
voltages and currents to all of the electrical
components, actuating valves and switches in a pre-
determined timed sequence, processing the electrical
signal from the temperature and conductivity cells, and
calculating total organic carbon concentration, total
carbon concentration and total inorganic carbon
concentration from the output of the temperature and
conductivity cells.

Next described is the typical operation of the
present invention as diagrammed in FIG. 1. The
peristaltic sampling pump 110 withdraws an aqueous sample
via the sample inlet conduit 10, at a desired flow rate
of 340 microliters per minute through the particulate
filter 12. Aqueous acid, such as phosphoric acid or
sulfuric acid, is introduced into the sample at the
fitting 16 at a controlled rate of approximately 1 uL/min
by the acid syringe pump 20. The desired pH of the
aqueous sample after acidification is about 2.

The acidification of the sample stream will
convert inorganic species to carbon dioxide, but will not
convert organic species to carbon dioxide. The
conversion of organic species to carbon dioxide requires
the U.V. (or other type) oxidation module.

Also introduced at the fitting 16 in the
preferred embodiment is an oxidizer such as persulfate as
discussed above, via the oxidizer syringe pump 28 and
oxidizer line 30. Rather than introducing oxidizer at a
constant rate, however, oxidizer is introduced at rates
that vary over an oxidation potential cycle as shown in

23

FIG. 3. At the start of a given oxidation potential
cycle, the oxidizer is introduced at a very low rate or
at a zero rate. The rate gradually increases over the
period of the cycle (210 seconds in the preferred
5   embodiment) until reaching a maximum rate. The cycle
then repeats.

The reason for varying the oxidation potential
is to ensure that the optimum oxidation is achieved at
some point in the cycle to produce the highest carbon
10   measurement downstream. If too little oxidation
potential is provided, the carbon could be incompletely
oxidized. In that event, insufficient carbon in the form
of carbon dioxide could pass through the semipermeable
membrane 58 in the gas transfer module 56 for downstream
15   measurement in the temperature and conductivity cell 94.
The result will be an inaccurately low total carbon
measurement. Conversely, if too much oxidation potential
is provided, oxygen bubbles will form which will
interrupt or lower the conductivity measurement in the
20   temperature and conductivity cell 94, also resulting in
an inaccurately low total carbon measurement. Thus the
accurate carbon measurement will be the one resulting
from the highest conductivity measurement in the
conductivity cells over the oxidation potential cycle.
25   As explained above, the variation in oxidation
potential can be achieved in several ways, in addition to
varying the rate of introducing chemical oxidizers such
as persulfate. Other approaches include varying the
intensity of a U.V. radiation source used as an oxidizer,
30   varying the residence time of the sample in a U.V.
radiation source, or varying the rate of electrolysis in

24

an electrolysis cell used to produce oxygen for
oxidation. The point of this step, regardless of the
approach chosen, is to vary the degree to which oxygen is
reacted with the sample or, in other words, to vary the
5   "oxidation potential."

The aqueous sample stream is split at fitting
18 into the first stream for the measurement of total
carbon and the second stream for the measurement of
inorganic carbon. The first stream enters the U.V.
10   oxidation reactor 46 where organic compounds are
converted to carbon dioxide and other products.
Simultaneously, the second stream enters the delay tubing
146. The two streams then enter their respective gas
transfer modules 56 and 156 simultaneously; that is, the
15   portion of the sample entering the first gas transfer
module 56 at a given moment was separated from the
portion of the sample entering the second gas transfer
module 156 at that same moment.

The effluent of the U.V. oxidation reactor 46
20   is directed via conduit 52 into the inlet of the first
gas transfer module 56, out through the outlet of the
first gas transfer module 56 through the peristaltic
sample pump 110 to a suitable waste container.
Similarly, the effluent of the delay tubing 146 is
25   directed via conduit 152 into the aqueous sample inlet of
the second gas transfer module 156, out through the
outlet of the second gas transfer module 156 through the
peristaltic sample pump 110 to the waste container.

A continuous supply of deionized water is
30   produced in the deionized water portion by passing an
aqueous stream of water through the mixed bed ion

exchange resins 66 by means of the circulating pump 70.
The deionized water flows in two loops: one is the total
carbon loop and the other is the inorganic carbon loop.
In the total carbon loop, deionized water flows from
5   fitting 74 via conduit 76 into the deionized water inlet
of the first gas transfer module 56. As the sample
stream passes on one side of the gas permeable membrane
58 of the gas transfer module 56, the carbon dioxide
formed upstream will diffuse across the gas permeable
10   membrane 58 into the deionized water sample on the
opposite side of the membrane 58, where the carbon
dioxide will be converted into ionic species. In the
inorganic carbon loop, deionized water flows from fitting
74 via conduit 80 into the deionized water inlet of the
15   second gas transfer module 156. As the sample stream
passes on one side of the gas permeable membrane 158 of
the second gas transfer module 156, the carbon dioxide
formed upstream by conversion of the inorganic carbon to
carbon dioxide in the acification step will diffuse
20   across the gas permeable membrane 158 into the deionized
water sample on the opposite side of the membrane 158,
where the carbon dioxide will be converted into ionic
species.

The increase in conductivity caused by the
25   presence of ionic species formed from carbon dioxide is
measured by the temperature and conductivity cells 94 and
194. The measured conductivity of the deionized water
sample can be directly related to the concentration of
carbon dioxide, and hence, the level of total carbon and
30   inorganic carbon compounds present in the aqueous sample
stream. Temperature measurements are also taken at or

proximate to the temperature and conductivity cells 94
and 194 so that the carbon determinations can take into
consideration the temperatures. The measurements at the
temperature and conductivity cells 94 and 194 can take

5   place virtually continuously or at periodic intervals
over the course of an oxidation potential cycle.

Once an oxidation potential period is
completed, the highest measured carbon is deemed the
correct measurement, and the other measurements are

10   deemed flawed due to insufficient oxidation or oxygen gas
production resulting in bubble formation. Thus a single
correct measurement is obtained for each cycle.
Sequential correct measurements are obtained in
sequential cycles. Thus a device utilizing 210 second

15   cycles can obtain a correct measurement approximately
every 210 seconds.

After the deionized water streams leave the
temperature and conductivity cells 94 and 194, they pass
through the restrictors 98 and 198. The restrictors 98

20   and 198 maintain a pressure differential. In a preferred
embodiment, they also function as deoxygenation modules
by allowing oxygen to diffuse through a gas permeable
wall to the atmosphere. The two deionized water streams
then join and flow into the ion exchange resin bed 66 via

25   the conduits 102 and 82, then to the pump 70, and back to
the splitting fitting 74 to complete the cycle. The
deionized water continuously circulates through the
exchange resin bed 66. Only a small fraction of that
circulation is tapped for circulation through the total

30   carbon loop and inorganic carbon loop.

EXAMPLE

In the depiction of FIG. 2, a 25 ppm KHP
standard solution was analyzed using several different
persulfate rates in a standard sample, using a Sievers
Model 800 device as described in U.S. Patent Nos.
5   5,132,094 and 5,443,991. That device is similar in
principle to the present invention, but it does not
automatically vary the oxidation potential over an
oxidation potential cycle. Therefore, the experiment was
conducted by using several different persulfate rates
10 successively, as shown in FIG. 2.

Because the U.V. light source in the oxidation
reactor is on during the entire cycle, some oxidation
takes place even when the oxidizer rate is 0, which is
reflected in the carbon determination shown in FIG. 2 of
15 almost 10 ppm at the 0 oxidizer rate.   The rate of
persulfate being added is then adjusted to 1 ul/min, 2
ul/min, and so on. The measured TOC increases, reaching
a maximum value when the persulfate rate is 4 ul/min.
Greater persulfate rates result in the formation of
20 oxygen bubbles in the sample stream and a depression in
the measured TOC. The cycle is then repeated, and again
the measured TOC increases to a maximum value and then
decreases as excess persulfate is added. The maximum TOC
value obtained during a cycle is used to calculate the
25 TOC of the sample stream.

EXAMPLE

FIG. 3 shows a graph of measured carbon and
persulfate flow rate versus time for a preferred
embodiment of the present invention, utilizing automatic
30 variable oxidation potential. The graph extends over
several oxidation potential cycles. It can be seen that

28

the persulfate flow rate in each cycle increases from
zero to approximately 6 ul/min. At the zero rate, there
is some carbon detected due to the oxidizing effect of
the U.V. radiation even in the absence of added

5   persulfate. As the oxidation potential is increased by
increasing the rate that persulfate is added to the
sample stream, the oxidation of the sample also
increases. This increasing oxidation results in
increasing organic carbon measurements, as more organic

10   carbon is converted to carbon dioxide. The peak organic
carbon measurement occurs at about 24 ppm, corresponding
to a persulfate flow rate of about 5.2 ul/min.

        As the persulfate flow rate is increased
further, the increased oxidation potential results in the

15   formation of oxygen gas bubbles. Those bubbles may
dilute the net average carbon dioxide concentration in
the same. In addition, they could diffuse through the
gas permeable membrane of the gas transfer module into
the deionized water stream and then into the temperature

20   and conductivity cell where they briefly partially or
wholly insulate the conductivity electrodes from the
deionized water stream, thereby interfering with the
conductivity measurement to produce an erroneously low
measurement. The erroneously low measurements are

25   reflected in the fall-off in the measured organic carbon
as the persulfate flow rate is increased from 5.2 to 6
ul/min, as shown in FIG. 3. The several cycles depicted
in FIG. 3 illustrate that these phenomena are quite
predictable and repeatable. In fact, for a given sample,

30   the cycles are virtually identical.

The embodiment described in the preceding
paragraphs contemplates an oxidizer rate that starts at a
minimum and gradually increases to a maximum over the
oxidizer cycle. However, it will be apparent that the
5   invention could as easily utilize some other oxidizer
rate profile such as a profile in which the rate starts
at a maximum and gradually declines to a minimum or the
rate varies in some other fashion. The important concept
is that the oxidizer rate does vary within a
10   predetermined range, to ensure that it is at the optimum
range at some point in the cycle.

The device as described herein may also
incorporate components for the removal of inorganic
carbon from the sample stream utilizing a membrane-based
15   carbon dioxide removal module in the sample stream. The
removal of inorganic carbon is beneficial in measuring
organic carbon in samples that contain a large amount of
inorganic carbon in relation to organic carbon, so that
the level of organic carbon determined by subtracting the
20   measured inorganic carbon from the measured total carbon
is not lost in the variability of the total carbon
measurement. This approach is described in some detail
in U.S. Patent No. 5,443,991 by Godec, et al.

It can be appreciated that the device and
25   method of the present invention can be used to make one
or more of several determinations. Total carbon can be
determined. Inorganic carbon can be determined.
Finally, organic carbon can be determined by subtracting
the inorganic carbon determination from the total carbon
30   determination.

The aspect of the invention in which the oxidation potential applied to a sample varies over an oxidation potential period can be utilized in other embodiments. One such other embodiment is shown in the block diagram of FIG. 4. An aqueous sample inlet 210 is in communication with a particle filter 212 for the removal of particulate matter that may be suspended in the aqueous sample stream. A filter outlet conduit 214 joins a fitting 216. An acid reagent ($6MH_3PO_4$ in the preferred embodiment) is delivered to the fitting 216 via a pump such as the acid syringe pump 220 through an acid line 222. The acid syringe pump 220 is driven by a motor 224 and worm gear 226 in the manner well known in the field of syringe pumps. The apparatus may also include an acid reservoir (not shown) for periodic replenishment of the acid syringe pump 220. Acidification of the sample stream by the introduction of acid at the fitting 216 serves to convert inorganic carbon compounds to carbon dioxide.

The outlet conduit 240 from the fitting 216 leads to a first gas transfer module 256. Like the gas transfer modules 56 and 156 of the embodiment of FIG. 1, the first gas transfer module 256 of FIG. 4 includes a carbon dioxide permeable membrane 258 positioned between the sample stream and a deionized water stream. The deionized water on the deionized water side is in a thin layer of approximately 0.01 to 0.02 inches and has a total volume of less than 150 ul to facilitate rapid response times. The deionized water can be from any of several sources. In the preferred embodiment of FIG. 4, the deionized water source 300 is a closed loop with a

circulating pump and a mixed bed of anion and cation ion
exchange resins similar to the deionized water closed
loop shown in the embodiment of FIG. 1.

5   Deionized water flows from the deionized water
source 300 into the first gas transfer module 256,
receives carbon dioxide permeating through the carbon
dioxide permeable membrane 258, and then flows to the
first temperature and conductivity cell 294. The first
temperature and conductivity cell 294 measures both the
10   temperature and conductivity cell of the stream of
deionized water with dissolved carbon dioxide, from which
the inorganic carbon concentration can be derived. The
first temperature and conductivity cell 294, as well as
the second temperature and conductivity cell 394
15   described below, have very small liquid volumes of less
than 10 ul. This very small liquid volume produces rapid
liquid turnover in the cell and consequently rapid
analysis and response times.

The stream leaves the first gas transfer module
20   256 and flows to a carbon dioxide degassification module
290 via conduit 295. The carbon dioxide degassification
module 290 preferably includes a length of carbon dioxide
permeable tubing positioned in a vacuum container.
Carbon dioxide permeates from the flowing stream through
25   the carbon dioxide permeable tubing into the vacuum
container. The vacuum is continuously or periodically
renewed by a vacuum pump (not shown) or other vacuum
producing source in communication with the container
interior. The exact dimensions and materials appropriate
30   for the carbon dioxide degassification module 290 depend
on the flow rate of the stream and the carbon

32

concentration in the stream.   In the preferred
embodiment, utilizing a flow rate of approximately 500
ul/min, the carbon dioxide permeable tubing is a
microporous material having an inside diameter of 280
microns and a length subjected to the vacuum of
approximately three inches.

It can be appreciated that the stream leaving
the gas transfer module 290 is essentially free of
inorganic carbon.   Substantially all the inorganic carbon
was converted to carbon dioxide in the upstream
acidification step, and the carbon dioxide was then
removed in the carbon dioxide degassification module 290.
At this point -- the conduit 250 from the outlet of the
carbon dioxide degassification module 290 -- the stream
still contains organic carbon, and the organic carbon has
not yet been measured.

The conduit 250 from the outlet of the carbon
dioxide degassification module leads to a fitting 260 for
the introduction of a chemical reagent to oxidize organic
carbons in the stream.   The chemical reagent in the
preferred embodiment is 15 percent $(NH_4)_2S_2O_8$ and is
delivered to the fitting 260 via an oxidizer syringe pump
228 through an oxidizer line 230.   The oxidizer syringe
pump 228 is driven by a motor 232 and worm gear 234 in
the conventional manner.   The apparatus may also include
an oxidizer reservoir (not shown) for periodic
replenishment of the oxidizer syringe pump 228.   The
stream then enters a U.V. oxidation reactor 246.   The
U.V. oxidation reactor 246 is preferably similar to the
U.V. oxidation reactor 46 described above in connection
with the embodiment of FIG. 1.

SUBSTITUTE SHEET (RULE 26)

As in the embodiment described above, this
embodiment oxides the stream using an oxidizer potential
that varies over an oxidation potential period. One
approach to varying the oxidization potential is to vary
the rate of introducing a chemical reagent oxidizer
through the oxidizer syringe pump 228 described in the
preceding paragraph. Other approaches to achieving that
objective in this embodiment, as in the other
embodiments, is to vary the rate of oxygen production in
an electrolysis cell, to vary the intensity of a U.V.
radiation oxidizer, or to vary the duration of exposure
of the stream to a U.V. radiation oxidizer.

The oxidation step, whether accomplished by a
chemical reagent oxidizer or by other means, oxidizes
organic carbon in the sample to produce dissolved carbon
dioxide. The concentration of the dissolved carbon
dioxide varies over the oxidation potential period
because the oxidation potential in the stream varies over
the oxidation potential period. The point of varying the
oxidation potential over the oxidation potential period
is to ensure that the oxidation potential reaches an
optimum at some point during the oxidation potential.
period. That optimum is when the organic carbon is
substantially completely oxidized, but no significant
oxygen bubbles have been formed. At that optimum, the
maximum possible carbon dioxide is produced without the
formation of interfering bubbles.

The stream, now with dissolved carbon dioxide
produced by the oxidation of organic carbon, flows
through conduit 270 into the second gas transfer module
356 similar to the first gas transfer module 256. The

second gas transfer module includes a carbon dioxide permeable membrane 358 positioned between the sample stream and another deionized water stream. This deionized water stream may be from the same source 300 as the deionized water stream used with the first gas transfer module 256, as shown in FIG. 4, or may be from a separate source. Deionized water flows from the deionized water source 300 into the second gas transfer module 356, receives carbon dioxide permeating through the carbon dioxide permeable membrane 358 of the second gas transfer module 356, and then flows to the second temperature conductivity cell 394.

The measured conductivity of the stream will vary over the oxidation potential period due to the variable oxidation over the oxidation potential period. That peak measured conductivity is deemed the accurate indicator of organic carbon concentration in the sample. Any lower measured conductivity in the presence of an oxidation potential lower than the oxidation potential that produced the peak is deemed due to incomplete oxidation of organic carbon in an insufficient oxidation potential. Any lower measured conductivity in the presence of an oxidation potential higher than the oxidation potential that produced the peak is deemed due to production of oxygen gas bubbles that interfere with the carbon dioxide measurement.

After leaving the second temperature and gas transfer module 356, the stream flows through pump 310 and into disposal line 312.

It can be appreciated that still other embodiments are possible utilizing the general approach

of varying the oxidation potential over an oxidation potential period. For example, the degassification module could utilize membrane separation of the stream from a basic stream as taught by U.S. Patent No.

5   5,132,094 by Godec, et al.

The apparatus thus makes a measurement of inorganic carbon concentration and a measurement of organic carbon concentration using a single stream. Total carbon can also be determined by adding the

10   measured inorganic carbon and measured organic carbon.

The present invention represents a significant improvement over the methods and apparatus existing for the measurement of total organic carbon, total inorganic carbon, and total carbon content of aqueous samples. The

15   present invention can be used for these rapid determinations in a wide range of samples, with minimal use of external chemical reagents, and without prior knowledge of the approximate carbon range in the sample. The use of a carbon dioxide selective membrane and

20   conductometric detection applied to the measurement of total organic carbon and total inorganic carbon concentrations in aqueous samples offers several advantages: 1) no purge gas, gas/liquid purge apparatus or drying system is required, 2) the conductometric

25   detection system provides excellent long-term calibration stability (over one year between calibrations) and minimal fouling or contamination since the sensor is only exposed to carbon dioxide in deionized water, 3) the size of the conductivity sensor can be sufficiently small that

30   accurate measurement in samples as small as 0.1 ml can be achieved, 4) membrane/conductometric detection provides a

large linear dynamic range, typically one to three orders
of magnitude greater than other techniques utilized for
the measurement of carbon dioxide in aqueous samples, 5)
the sensitivity of the carbon dioxide sensor and

5   conductivity detector is substantially better than in
other techniques, 6) no sample clean-up or dilution is
required, 7) if used with an inorganic carbon removal
module the device can accurately measure very low
concentrations of organic carbon even in the presence of

10   relatively high concentrations of inorganic carbon, 8)
the membrane-based sensing system minimizes interference
from other gasses, and 9) the use of thin sample layers
and low volume components facilitates rapid response to
allow practical use in commercial applications.

15

CLAIMS

What is claimed is:

1.   A method for measuring carbon in an aqueous sample, comprising the steps of: establishing a flowing stream of said sample; oxidizing carbon in the sample stream using an oxidation potential that varies during an oxidation potential period to produce concentrations of carbon dioxide in the stream that vary during the oxidation potential period; measuring a concentration of carbon dioxide in the stream at a plurality of times during the oxidation potential period; determining the highest measurement of the concentration of carbon dioxide in the stream during the oxidation potential period; and determining the carbon concentration in the sample from said highest measurement.

2.   The method of claim 1, wherein the step of oxidizing carbon includes introducing an oxidizer reagent to the sample at an introducing rate that varies during the oxidation potential period.

3.   The method of claim 1, wherein the step of oxidizing carbon includes irradiating the sample with ultraviolet radiation.

4.   The method of claim 3, wherein said step of irradiating the sample includes applying radiation from a source chosen from the group consisting of a mercury vapor lamp and an excimer lamp.

5.   The method of claim 1, wherein the step of oxidizing carbon includes introducing the sample into an electrolysis cell in which the oxidation potential varies over the oxidation potential period.

38

6.   The method of claim 1, wherein the step of measuring a concentration of carbon dioxide includes applying the sample to one side of a carbon dioxide permeable membrane; applying deionized water to an opposite side of the membrane; allowing carbon dioxide to permeate from the sample through the carbon dioxide permeable membrane and into the deionized water; and measuring the conductivity of the deionized water with carbon dioxide permeated from the sample through the carbon dioxide permeable membrane.

7.   The method of claim 6, wherein the sample is in a layer less than .06 inches thick on said one side of the carbon dioxide permeable membrane, and the volume of said layer is less than 1,000 ul.

8.   The method of claim 6 wherein the sample flows continuously past said one side of the membrane during the oxidizer period in a first direction and the water flows continuously past said opposite side of the membrane during the oxidizer period in a second direction opposite the first direction.

9.   The method of claim 8, wherein the deionized water flows in a closed loop, and said loop includes a water deionizer.

10.   The method of claim 9 wherein the deionized water on said opposite side of the carbon dioxide permeable membrane is maintained at a pressure higher than said sample on said one side of the carbon dioxide permeable membrane.

11.   The method of claim 10, wherein the deionized water applied to said opposite side of the membrane, with carbon dioxide permeated from the sample

39

through the carbon dioxide permeable membrane, flows past
the membrane and into a conductivity cell.

12.   The method of claim 11, wherein the
conductivity cell includes a temperature sensor and has a
liquid volume of less than 500 ul.

13.   The method of claim 1, wherein said
oxidizing step includes converting organic carbon to
carbon dioxide, and further comprising acidifying the
stream to convert inorganic carbon to carbon dioxide.

14.   A method for measuring total carbon in an
aqueous sample, comprising the steps of: establishing a
flowing stream of said sample; adding acid to the stream
to convert inorganic carbon in the stream to carbon
dioxide; oxidizing carbon in the stream using an
oxidation potential that varies during an oxidation
potential period to produce concentrations of carbon
dioxide in the stream that vary during the oxidation
potential period; measuring a concentration of carbon
dioxide in the stream at a plurality of times during the
oxidation potential period; determining the highest
measurement of the concentration of carbon dioxide in the
stream during the oxidation potential period; and
determining the total carbon concentration in the sample
from said highest measurement.

15.   The method of claim 14, wherein said
oxidation potential increases from a minimum rate to a
maximum rate during the oxidation potential period.

16.   The method of claim 14, wherein said step
of measuring a concentration of carbon dioxide in the
stream includes flowing the stream over a carbon dioxide
permeable membrane separating the stream from deionized

water to allow carbon dioxide to permeate from the stream
through the carbon dioxide permeable membrane and into
the deionized water stream, and measuring the
conductivity of the deionized water with carbon dioxide.

5   17.   The method of claim 14, further comprising
determining the inorganic carbon concentration in the
sample by measuring the concentration of said carbon
dioxide produced by adding acid to the stream, prior to
said step of oxidizing carbon in the stream using an

10   oxidation potential that varies during an oxidation
potential period.

          18.   The method of claim 17, further comprising
removing carbon dioxide from the stream between said step
of adding acid and said step of oxidizing carbon in the

15   stream using an oxidation potential that varies during an
oxidation potential period.

          19.   A method of measuring both total carbon
and inorganic carbon in a sample, comprising: acidifying
the sample to convert inorganic carbon to carbon dioxide;

20   measuring the carbon dioxide produced by said conversion
from inorganic carbon to carbon dioxide; determining the
inorganic carbon concentration in the sample from said`
measurement of carbon dioxide produced by conversion from
inorganic carbon to carbon dioxide; oxidizing organic

25   carbon in the sample using an oxidation potential that
varies during an oxidation potential period to produce
concentrations of carbon dioxide that vary during the
oxidation potential period; determining the highest
measurement of the concentration of carbon dioxide during

30   the oxidation potential period; and determining the total

carbon concentration in the sample from said highest measurement.

20. The method of claim 19, further comprising determining the concentration of total organic carbon in the sample by subtracting the determined concentration of inorganic carbon from the determined concentration of total carbon.

21. The method of claim 19, wherein after the acidification step the sample stream is split into a stream for measurement of inorganic carbon and a stream for measurement of total carbon.

22. The method of claim 21, wherein the measurement of total carbon is by measuring the carbon dioxide in the total carbon stream and the measurement of inorganic carbon is by measuring carbon dioxide in the inorganic carbon stream.

23. The method of claim 22, wherein the measurement of inorganic carbon and the measurement of total carbon occur substantially simultaneously.

24. The method of claim 22, wherein the measuring of carbon dioxide in the total carbon stream is by flowing the total carbon stream past a first carbon dioxide permeable membrane separating the total carbon stream from a first deionized water stream, allowing carbon dioxide to permeate from the total carbon stream through the first carbon dioxide permeable membrane and into the first deionized water stream, and measuring the conductivity of the first deionized water stream with carbon dioxide permeated through the first carbon dioxide permeable membrane.

25. The method of claim 24, wherein the total carbon stream is in a layer on the first carbon dioxide permeable membrane less than 0.06 inches thick and has a volume in said layer of less than 1,000 ul.

26. The method of claim 24, wherein the measuring of carbon dioxide in the inorganic carbon stream is by flowing the inorganic carbon stream past a second carbon dioxide permeable membrane separating the inorganic carbon stream from a second deionized water stream, allowing carbon dioxide to permeate from the inorganic carbon stream through the second membrane and into the second deionized water stream, and measuring the conductivity of the second deionized water stream with carbon dioxide permeated through the second carbon dioxide permeable membrane.

27. The method of claim 26, wherein the first deionized water stream and second deionized water stream join and flow through a deionizer and then separate to flow back to the first and second gas permeable membranes.

28. An apparatus for the measurement of carbon in an aqueous sample, comprising: an oxidation reactor that varies an oxidation potential during an oxidation potential period to produce carbon dioxide concentrations that vary during the oxidation potential period; and a first carbon dioxide sensor to measure the amount of carbon dioxide in the sample at a plurality of times during the oxidation potential period.

29. The apparatus of claim 28, wherein the oxidation reactor includes a reagent pump to pump an

oxidizing reagent into the sample stream at a rate that varies over the oxidation potential period.

30. The apparatus of claim 28, further comprising an ultraviolet light source to irradiate the sample to assist in the oxidation of the sample.

31. The apparatus of claim 28, wherein the first carbon dioxide sensor includes a carbon dioxide permeable membrane separating the sample from deionized water, and a conductivity cell, whereby carbon dioxide may permeate from the sample through the membrane and into the deionized water to be measured in the conductivity cell at a known temperature.

32. The apparatus of claim 31, wherein the carbon dioxide permeable membrane defines on one side of the carbon dioxide permeable membrane a sample layer less than 0.06 inches thick and less than 1,000 ul in volume.

33. The apparatus of claim 31, wherein the conductivity cell includes a temperature sensor and has a volume of less than 500 ul.

34. The apparatus of claim 31, wherein the first carbon dioxide sensor includes a closed loop for said deionized water, whereby the deionized water flows past the carbon dioxide permeable membrane, into the conductivity cell, and returns to the carbon dioxide permeable membrane.

35. The apparatus of claim 34, wherein the loop includes a deionizer.

36. The apparatus of claim 34, further comprising an acidifier for acidifying the sample to covert inorganic carbon to carbon dioxide.

37.   The apparatus of claim 28, wherein the first carbon dioxide sensor includes a gas transfer module to transfer carbon dioxide from the sample to deionized water and a conductivity cell to measure the conductivity of the deionized water with carbon dioxide.

38.   The apparatus of claim 28, further comprising a set of conduits to contain a flowing stream of the sample, the oxidation reactor and first carbon dioxide sensor being in fluid communication with the set of conduits.

39.   The apparatus of claim 37, further comprising an acidifier in fluid communication with the set of conduits to add acid to the stream to convert inorganic carbon to carbon dioxide.

40.   The apparatus of claim 39, further comprising a second carbon dioxide sensor to measure carbon dioxide in the stream, the second carbon dioxide sensor being in fluid communication with the set of conduits downstream from the acidifier.

41.   The apparatus of claim 40, wherein the second carbon dioxide sensor includes a gas transfer module to transfer carbon dioxide from the sample to deionized water and a conductivity cell to measure the conductivity of the deionized water with carbon dioxide.

42.   The apparatus of claim 40, further comprising a carbon dioxide remover, the carbon dioxide remover being in fluid communication with the set of conduits between the first carbon dioxide sensor and the second carbon dioxide sensor.

43.   The apparatus of claim 42, wherein the second carbon dioxide sensor is downstream from the

acidifier, the carbon dioxide remover is downstream from the second carbon dioxide sensor, the oxidation reactor is downstream from the carbon dioxide remover, and the first carbon dioxide sensor is downstream from the oxidation reactor.

44. The apparatus of claim 28, further comprising a first set of conduits to contain a first flowing stream of the sample; a second set of conduits to contain a second flowing stream of the sample in parallel with the first stream; the first carbon dioxide sensor being in fluid communication with the first set of conduits; and further comprising a second carbon dioxide sensor in fluid communication with the second set of conduits.

45. The apparatus of claim 44, further comprising an ultraviolet light source to irradiate the first stream downstream from the oxidation reactor.

46. The apparatus of claim 45, wherein the first carbon dioxide sensor includes a first carbon dioxide permeable membrane to separate the first stream from deionized water, and a first conductivity cell, whereby carbon dioxide may permeate from the first stream through the second membrane and into the deionized water to be measured in the first conductivity cell at a known temperature.

47. The apparatus of claim 46, wherein the second carbon dioxide sensor includes a second carbon dioxide permeable membrane to separate the second stream from deionized water, and a second conductivity cell, whereby carbon dioxide may permeate from the second stream through the second membrane and into the deionized

water to be measured in the second conductivity cell at a
known temperature.

48.   The apparatus of claim 47, further
comprising a set of deionized water conduits to contain
the deionized water into which carbon dioxide permeates
from the first stream and the deionized water into which
carbon dioxide permeates from the second stream.

49.   The apparatus of claim 48, further
comprising a deionized water source in communication with
said deionized water set of conduits.

50.   The apparatus of claim 49, wherein said
deionized water source includes a water deionizer, and
further comprising a circulating pump to circulate water
through the deionizer and through the first carbon
dioxide sensor and second carbon dioxide sensor.

51.   The apparatus of claim 50, wherein said
first set of conduits and said second set of conduits
split a main sample stream, and said oxidation reactor
includes an oxidizer reagent pump in communication with
the main sample stream.

52.   The apparatus of claim 51, further
comprising an acid source in communication with the main
sample stream.

53.   The apparatus of claim 52, wherein the
second set of conduits includes a set of dela
y tubing to delay the flow of the second stream for a
period of time substantially equal to a period of time
for the first stream to flow past the ultraviolet light
source.

54.   A method of measuring inorganic carbon and
organic carbon in a sample, comprising establishing a

flowing stream of the sample; acidifying the stream to
convert inorganic carbon to carbon dioxide; oxidizing
organic carbon in the stream to produce carbon dioxide
using an oxidation potential that varies during an
5   oxidation potential period to produce concentrations of
carbon dioxide in the stream that vary during the
oxidation potential period; determining the highest
concentration of carbon dioxide in the stream during the
oxidation potential period; and determining the carbon
10   concentration in the sample from said highest
concentration of carbon dioxide.

55.   The method of claim 54, further comprising
measuring the carbon dioxide in the stream after said
acidifying step and before said oxidizing step; and
15   relating said measured carbon dioxide to the inorganic
carbon concentration in the sample.

56.   The method of claim 54, further comprising
removing carbon dioxide from the stream, said step of
removing carbon dioxide from the stream occurring after
20   said step of measuring the carbon dioxide in the stream
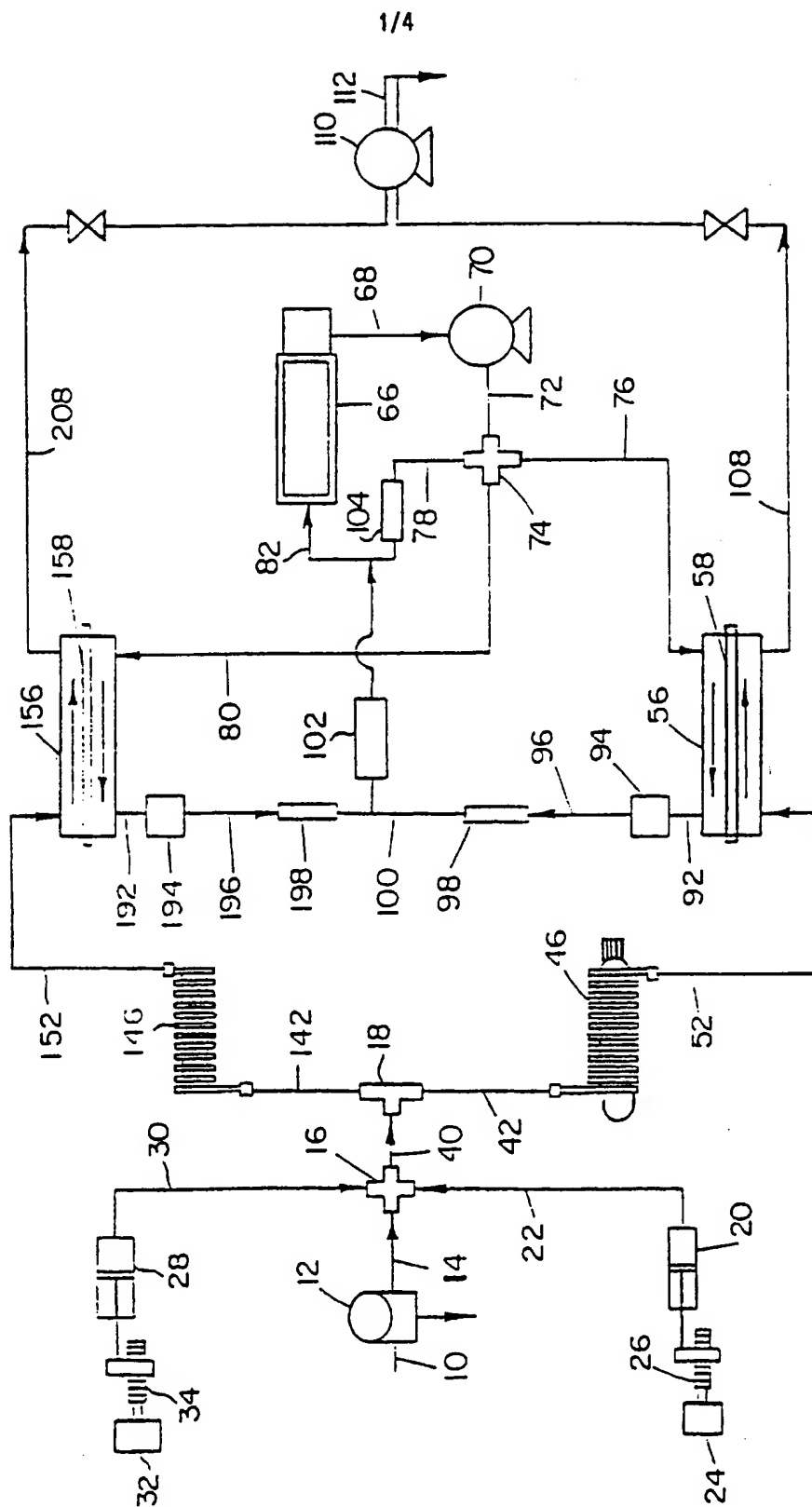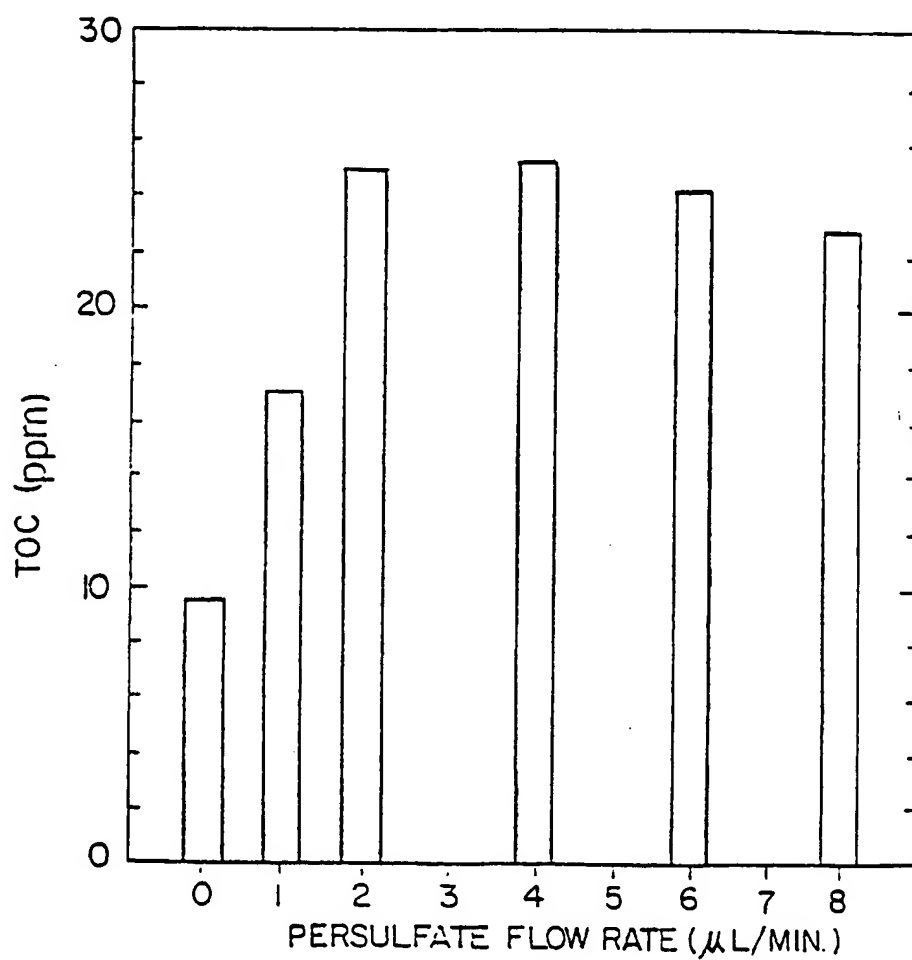and before said step of oxidizing the stream.
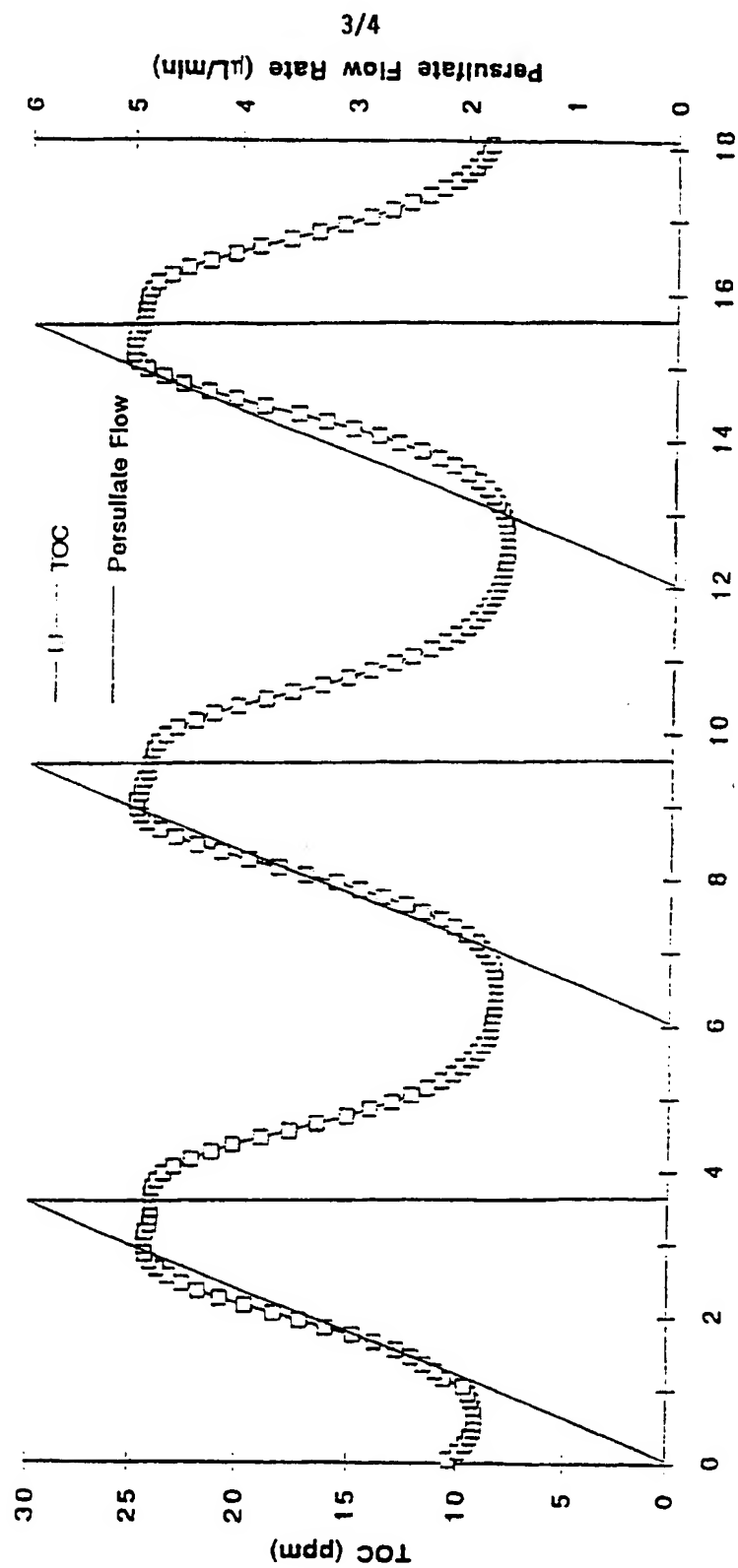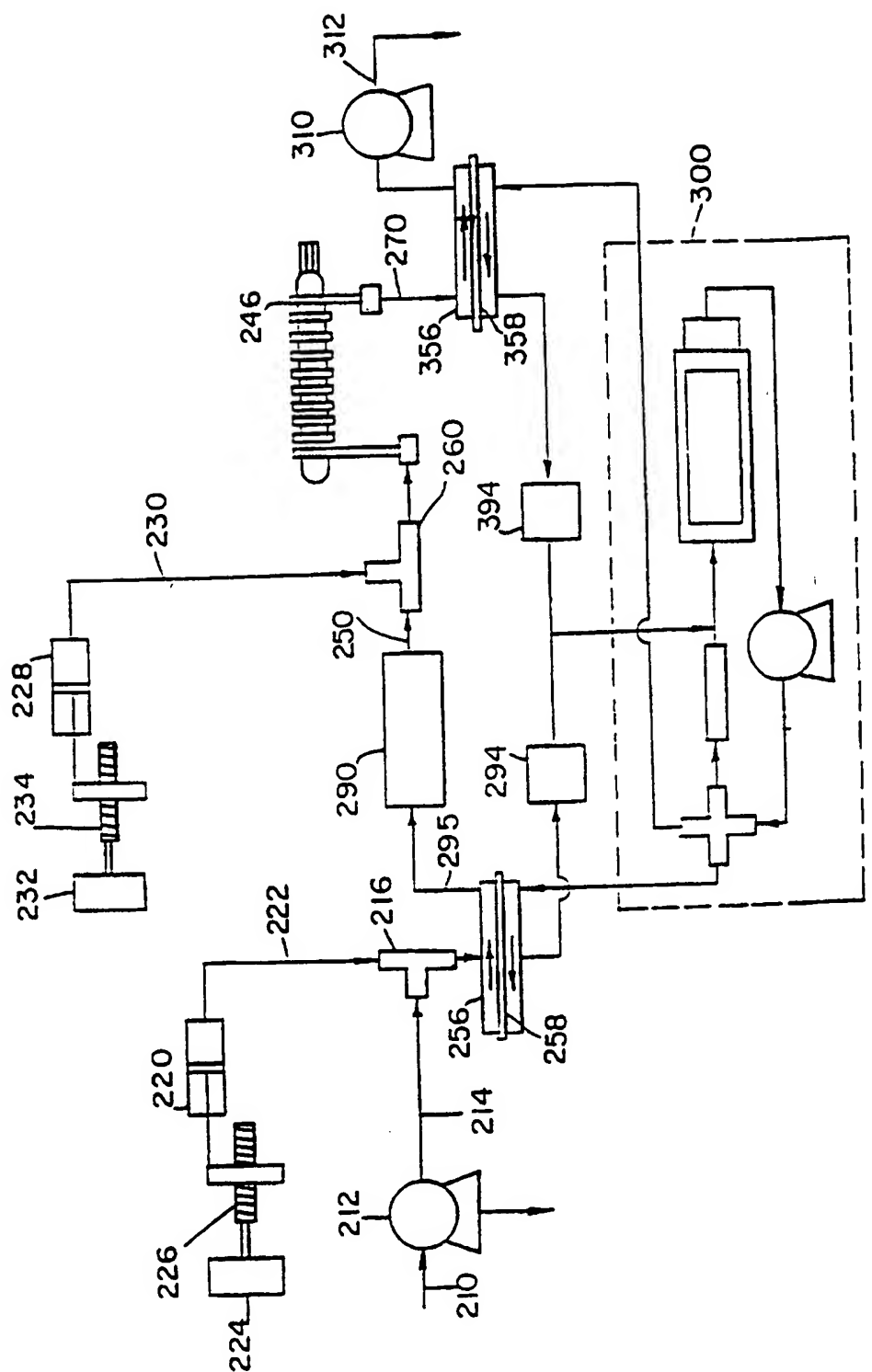
FIG.1

FIG. 2

3/4

FIG. 3

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/19217

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :G01N 33/00

US CL :436/146

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 436/145, 146, 147, 148, 149, 152; 422/78, 79, 80, 82.02, 82.12, 186.3, 186.04, 186.05

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,047,212 A (BLADES et al) 10 September 1991, see entire document.	1, 28
X	US 4,868,127 A (BLADES et al) 19 September 1989, see entire document.	1, 28
Y	US 4,666,860 A (BLADES et al) 19 May 1987, see entire document.	2-27, 29-56
Y	US 4,626,413 A (BLADES et al) 02 December 1986, see entire document.	2-27, 29-56
Y	US 4,293,522 A (WINKLER) 06 October 1981, see entire document.	2-27, 29-56
Y	US 4,209,299 A (CARLSON) 24 June 1980, see entire document.	2-27, 29-56

[X] Further documents are listed in the continuation of Box C.   [ ] See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 MARCH 1997	1 4 APR 1997

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,619,902 A (BERNARD) 28 October 1986, see entire document.	1-56
A	US 4,277,438 A (EJZAK) 07 July 1981, see entire document.	1-56
A	US 3,958,941 A (REGAN) 25 May 1976, see entire document.	1-56
A	US 4,775,634 A (SIENKIEWICZ) 04 October 1988, see entire document.	1-56